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**AUTHOR(S): L. J. Collins, T-4  
B. I. Schneider, T-12**

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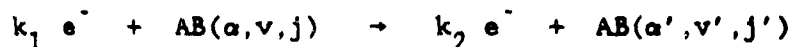
## RECENT ADVANCES IN THE THEORY OF ELECTRON IMPACT EXCITATION OF MOLECULES

L. A. Collins and B.I. Schneider

T-Division, Los Alamos National Laboratory, Los Alamos, NM, 87545, U.S.A

### 1. INTRODUCTION

Molecules are "pesky" and highly excitable little "critters," especially in the presence of electrons. In addition to electronic transitions with their direct analogue to atoms, molecules have the habit of vibrationally and rotationally exciting. Therefore, the full scope of the excitation process becomes:



where  $(\alpha, v, j)$  labels an electronic state of the target molecule in a particular vibrational and rotational mode. At present, we do not have any methods that can treat this problem in all of its glory. Fortunately, the characteristic times for the molecular transitions and the collision are such that approximations can usually be made for the nuclear motion. Different types of transitions can then be treated at different levels of sophistication. For example, the characteristic times for rotation are usually quite slow compared with the duration of the collision. In this case, we fix the molecule in space and perform our scattering calculations for this orientation. Excitation quantities, such as cross sections, can be found by averaging over the proper rotational eigenfunctions of the target molecule. This particular construction is valid for a wide range of energies and systems but does experience problems when the energy of the continuum electron is quite small as near thresholds, when the electron becomes trapped in a resonance state of the compound system, or when the electron experiences a very long-range interaction. For these situations, we can relax the fixed orientation approximation by the use of simple frame-transformations or rotational close-coupling methods. The vibrational times are generally shorter than the rotation and therefore closer to those for the collision. However, sudden approximations for the electron motion still have a wide range of validity. Collisional quantities are again determined by averaging the scattering amplitude, calculated at a series of fixed internuclear distances, over the vibrational states of the molecule. Complications for this adiabatic-nuclei approach to vibration arise in many of the same cases mentioned for rotation and can be rectified by similar techniques. Finally, if the energy of the incident electron is sufficient, the molecule can experience electronic excitations. Such excitations can also be associated with attachment, recombination, and dissociative processes(1). Since rotation and vibration have recently received rather extensive treatments(2-5), we shall concentrate on electronic excitations. In addition, we shall emphasize the low-energy(<

100eV) regime, which has received the greatest recent attention.

The past few years have witnessed an explosion in the methods to treat electronic-excitation processes in electron-molecule collisions. This is most readily seen by consulting recent reviews. In 1984, Trajmar and Cartwright(6) gave a comprehensive report of the status of the field. At that time, only three close-coupling calculations applied to two molecules, hydrogen and nitrogen, were listed. Even these pioneering *ab initio* treatments contained restrictions on the full formulation. Within just the past three years a number of methods, which had shown great success for elastic collisions, were extended to the multichannel level. Up to ten-state calculations have been performed on the hydrogenic systems, while excitation cross sections have been determined for such open-shell targets as oxygen. These accomplishments mark only the opening stage of exploration since all the methods have the potential to address larger systems and more complicated processes. With the ability to treat static, exchange, and correlation effects on an equal footing, we can now use these techniques to probe the intricacies of the electron-molecule interactions. In addition, significant advances have been made in the development of models. These models appear to possess a flexibility, in certain cases, to treat many-channel problems and to extend the range of systems that can be examined. Therefore, we are at a most propitious time in the theory of electronic excitation of molecules.

The earliest calculations of electronic excitation invoked the Born approximation(BA) with very simple expressions of the interaction potentials (7). As molecular structure methods advanced, we could determine more elaborate forms for the coupling matrix elements and could, using simple models, even introduce exchange effects into the first-order scattering(8-10). In this same vein, impact approximations, based on semiclassical treatments, were developed(11,12). Still all of these forms used rather crude representations of the scattering wavefunction. Results for the integral cross sections might be within a factor of two to five of experiment; however, differential cross sections(DCS) in certain angular regions were sometimes orders of magnitude in error. The distorted wave(DW) approach(13,14) marked a distinct improvement. We could now account for some effects of the target molecule on the scattered electron. Much better agreement was found in the DCS with experiment, especially for the optically allowed transitions, which depended on the direct static coupling and high angular momenta. Problems, however, persisted for the forbidden transitions since the coupling is primarily provided by the exchange terms. This situation was rectified to some extent by the advent of full close-coupling programs(15,16) in the 1970's although they could only handle a very limited number of states. Exchange effects were included as well as balanced coupling. However, not until the last few years have methods advanced so that a full and systematic treatment of the entire electronic-excitation process can be realized(17). The field is in an inchoate phase with the major areas of interest just being explored.

In this article, we present an overview of this rapidly developing field. In the next section, we shall briefly and schematically develop some of the basic formalism necessary to explicate the collisional process. The emphasis will be on general features and not specific details. We follow this with a section considering several examples of electronic-excitation processes, which illustrate some interesting aspects of these collisions. We conclude with a status report and some predictions about the future directions of the field.

## 2. A LITTLE FORMALISM

### 2.1 Basic Formulation

In this section, we develop some of the basic procedures employed in solving the electron-molecule scattering problem. We shall invoke several approximations or constraints in order to simplify the formulation. These approximations can be relaxed by various prescriptions and are not overly restrictive. First, we shall assume that the molecule is fixed at a given internuclear separation,  $R$ , during the collision. This "fixed-nuclei" restraint is a sudden approximation applied to the continuum electron and an adiabatic one with respect to the nuclear motion. We can then, for example, determine vibrational-excitation quantities by calculating the scattering amplitude at a number of fixed  $R$ -values and averaging over the eigenfunctions of the nuclear motion. This adiabatic-nuclei (AN) approximation (18) can be relaxed by several procedures including frame-transformations (19), vibrational-electronic close-coupling (20), approximations to the nonadiabatic terms (21), and projection-operator techniques (22). In addition, much of the rich structure in the collisional cross section, due to rotation, vibration, and electronic processes, can be produced from limited theoretical or experimental information by multichannel quantum defect methods (23). Second, we shall explicitly account for spin in the antisymmetric form of the system wavefunction; however, we shall treat it implicitly through most of the formulation. In all of the methods, spin is properly included. With these provisions, we are ready to attack the electron scattering process.

We describe the collision of an electron with a diatomic molecule of  $n$  electrons by a many-body Schrodinger equation of the form

$$H \psi(1 \dots n+1) = E \psi(1 \dots n+1) \quad , \quad (1)$$

where

$$H = T + V + H_{\text{mol}} \quad ; \quad (2a)$$

$$V = V_{ee} + V_{en} \quad . \quad (2b)$$

The kinetic energy of the continuum electron is given by  $T$ , the interaction of the incident electron with the target electrons (nuclei) by  $V_{ee}$  ( $V_{en}$ ), and the hamiltonian for the  $n$  molecular electrons by  $H_{\text{mol}}$ . We employ the shorthand notation  $(1 \dots m)$  to represent the full spatial and spin coordinates of  $m$  particles. We reduce this many-body formulation to an effective one-particle problem by expanding in terms of a complete set of eigenstates of the target molecule as

$$\psi(1 \dots n+1) = \sum_{\alpha=1}^{\infty} A(\alpha) F_{\alpha}(n+1) \phi_{\alpha}(1 \dots n) \quad (3a)$$

where

$$H_{\text{mol}} \phi_{\alpha}(1 \dots n) = \epsilon_{\alpha} \phi_{\alpha}(1 \dots n) \quad , \quad (3b)$$

A represents the antisymmetry operator, which guarantees that the total system wavefunction obeys the Pauli exclusion principle, and  $\alpha$  labels a particular electronic state of the target. We recall that the scattering function F has an implicit dependence on the fixed internuclear distance R.

We derive an equation for the scattering function, F, by substituting Eq.(3a) into Eq.(1), multiplying through by the complex conjugate of a representative state, and integrating over all target coordinates. The resulting set of coupled integrodifferential equations(IDE's) has the form:

$$[\nabla^2 + k_\alpha^2] F_\alpha(\vec{r}) = \sum_\beta [V_{\alpha\beta}(\vec{r}) F_\beta(\vec{r}) + V_{\alpha\beta}^{\text{ex}}(\vec{r})] \quad (4a)$$

where

$$V_{\alpha\beta}^{\text{ex}}(\vec{r}) = \int W_{\alpha\beta}(\vec{r}|\vec{r}_1) F_\beta(\vec{r}_1) d\vec{r}_1 \quad (4b)$$

$$k_\alpha^2 = 2(E - \epsilon_\alpha) \quad ,$$

and  $\vec{r}$  represents the spatial coordinates of the continuum electron. The direct electrostatic interaction is given by  $V_{\alpha\beta}$  and is simply found by integrating V over two target wavefunctions,  $\langle\alpha|V|\beta\rangle$ . Since the static interaction is local, we determine this term from the results of molecular-structure calculations, independently of the scattering solution. On the other hand, evaluation of the exchange component, given by the second term in Eq.(4a), depends on knowledge of F. The term is nonlocal and energy dependent and contains both one- and two- electron contributions. These exchange terms are purely quantum mechanical in nature, arising from the constraints imposed by the Pauli principle, and greatly complicate the solution of the scattering equations. In practical applications, we make the close-coupling(CC) approximation and truncate the summation in Eq.(3a) at a finite number of terms,  $n_c$ . We add terms until successive values of certain scattering parameters converge to within a given tolerance. Once the solution is found, we extract the scattering information, such as the reactance, scattering, or transition matrices, K, S, and T respectively, by matching to the known form of the asymptotic wavefunctions. From these matrices, we generate the relevant cross sections(2).

Since the expansion in terms of target states can be slow, we commonly represent the solution as

$$\psi(1..n+1) = \sum_{\alpha=1}^m A(F_\alpha(n+1) \phi_\alpha(1..n)) + \sum_q d_q \chi_q(1..n+1) \quad (5)$$

where the first term is the same as Eq (3a) except over a limited number of states, and the second term is added for completeness. We generally impose the strong orthogonality constraint by which we force the orbitals used to represent  $\phi$  and  $\chi$  to be orthogonal to the continuum solution. This condition rarely holds in excitation, which involves open shells, and must be relaxed by a proper choice of the  $\chi$  functions. However, we do gain a substantial simplification to the scattering equation by imposing this constraint since many of the one-electron terms vanish. In addition, we usually restrict the first sum to those states for which we desire scattering information. In this

case, the number of terms is usually much smaller than in the CC approach ( $m < n_c$ ). The "correlation" functions  $\chi$  represent the compound states of electron+molecule system and are used to restore some of the effects omitted from the truncated sum of the first term. In a manner analogous to our derivation of Eq.(4), we use the expansion in Eq.(5) to reduce the many-body Schroedinger equation to an effective one-particle case by selectively multiplying by the target and correlation functions. We now obtain two sets of IDE's, one for  $F$  and one for the  $d$  coefficients. We eliminate these coefficients and obtain an equation of the form of (4) except for a limited range of states. The nonlocal term  $W$  is now more complicated, being an effective optical potential involving both  $\phi$  and  $\chi$ . Several advantages arise from this approach, which is closely akin to the Feshbach projection-operator(24) formulation: 1) we need only solve the complicated set of IDE's for a limited number of channels,  $m$ , which is smaller than needed to converge the standard CC, and 2) the correlation functions, in some constructions, can be determined independently, usually through a configuration-interaction(CI) bound-state program.

We can derive the basic forms of the collisional approximations from Eq.(4). As they now stand, these equations represent the full treatment of the static, exchange, and correlation effects. Systematically increasing the target or correlation function expansion in Eq.(5) will lead to a complete representation of the scattering. Therefore, to within computational constraints, the methods based on these approaches are "exact." The simplest form of the Born approximation for neutral targets comes from neglecting all of the potential terms and representing the scattering as a free particle. The excitation process is given in first order by simply sandwiching the coupling matrix element between the plane wave solutions for the initial and final electron energies,  $k_\alpha$  and  $k_\beta$  respectively. For example, the transition matrix( $\alpha \rightarrow \beta$ ) has the general form -

$$T_{\alpha\beta} = \alpha \left| \langle k_\alpha | V_{\alpha\beta} | k_\beta \rangle \right|^2$$

Exchange effects can also be introduced into this expression through various approximations such as the Ockur(8) and Rudge(9). In the distorted -wave approaches(13), we limit the expansion to just the two states and set the back-coupling potential term  $V_{\beta\alpha}$  to zero. We thus take into account the diagonal distortion terms and coupling in one direction.

## 2.1 Methods of Solution

Since comprehensive reviews of the methods appear elsewhere(2,17,23,26), we present only a brief description of the numerous techniques that have been devised to solve Eq.(4). In the past, two distinct approaches evolved based on numerical and square-integrable( $L^2$ ) basis-set prescriptions. This distinction has blurred as many methods now conflate the procedures. The numerical approach is usually marked by a further expansion of the scattering solutions in partial waves. This single-center (SC) expansion allows the angular dependence to be removed, and a set of radial IDE's to be solved by standard propagation techniques(15). In other approaches these sets were converted to integral equations and solved either by propagation or by linear algebraic(LA) procedures. In the latter case(27,28), we derive a set of matrix equations by imposing a discrete quadrature on the functions and integrals. Such matrix approaches utilize the full power of the new vector and multi-tasking computers. The SC expansion gives an accurate description of the scattering wavefunction in the intermediate and far spatial ranges. However, near the

nuclei, many expansion terms are needed to represent the function. Still, unlike in bound-state problems, SC expansions have been systematically converged to give accurate scattering information for a wide variety of systems since the nuclear region does not play as dominant a role as for bound states.

The second approach utilizes an expansion in terms of a known set of square-integrable functions of the spatial variables. These functions may be analytical, such as Slater- or Gaussian- type orbitals, or numerical solutions to a model potential. The coefficients of this expansion are usually found by a variational prescription. Two basic approaches have emerged. In the first, illustrated by the R-matrix(RM) method(29-33), we divide space into two regions. In the inner region, we solve the full scattering problem given by Eq.(4) subject to arbitrary boundary conditions at the surface. The imposition of these boundary conditions leads to an eigenvalue problem in the inner zone with the coefficients of the basis expansion found by standard diagonalization procedures. The R-matrix is expressed in terms of these eigenfunctions, and the scattering information found by matching to solutions, whose asymptotic behavior is known in the outer region. The method is closely akin to finite-volume variational schemes(34). An alternative approach is to utilize a trial function that spans all space. Such prescriptions as the Kohn(35), which employs functions that satisfy the asymptotic boundary conditions, and the Schwinger(SV) have been used. Since the basis functions in the SV(36,37) and related C-functional(38) methods need not conform to the long-range scattering behavior, limited-range square-integrable functions can be effectively employed. While these square integrable approaches give an excellent representation of the function near the nuclei, they have difficulty representing the oscillatory nature in the outer regions. This can be mollified to some extent by using continuum-like functions or going to complex basis functions.

In the above paragraphs, we have described various ab initio approaches in which the static, exchange, and correlations effects are treated on the same footing within some reasonably complete formulation. Such methods have had reasonable successes for small molecular systems. In the near future, to go beyond second-row systems will require some approximations to be made to the important interactions. Models that represent the exchange and correlation effects by local terms have been successfully applied to elastic collisions; however, they have had but limited applications to electronic excitation. A new approach that shows promise is the effective range(ERT) theory, which has also been applied to rotation and vibration(39). In the ERT(40), we again partition space. In the inner region, we use bound-state programs to develop a form of the negative-ion wavefunction. This is then matched at some boundary to a superposition of uncoupled scattering functions that represent the allowed channels. Such an approach is especially appropriate for excitation processes dominated by a shape resonance. While we have concentrated on the low-energy regime, we should remember that approximate approaches such as the Born and distorted wave give reasonably reliable results at higher scattering energies.

### 3. REPRESENTATIVE SYSTEMS

In this section, we present several representative examples of the types of excitation processes that can be examined and the interactions that can now be studied.



### 3.1 Feshbach Resonances $H_2^+$

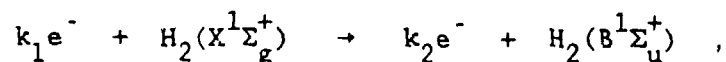
The hydrogen molecular ion forms the simplest target system. Since the full interaction involves only two electrons, we expect a rather detailed treatment is possible. We concentrate on one particular aspect of the collision by investigating the region below the first electronic threshold. While only elastic scattering is possible, we encounter series of Feshbach resonances, which arise from the temporary trapping of the continuum electron in a doubly-excited compound state of molecular hydrogen. This trapping or time-delay( $\tau$ ) is characterized by a width( $1/\tau$ ); the larger the width, the shorter the confinement time. For an ion, we have Rydberg series of the resonances converging on the various excitation thresholds. For example, if we consider a total scattering symmetry of  $^1\Pi_u$ , we have a series[1] of the form  $1\sigma_u n\pi_u$  beneath the first excited state of the ion( $1\sigma_u$ ). We also have the series[2],  $1\pi_u^+ n\sigma_g$ , associated with the second state. As we vary the internuclear separation,  $R$ , the relative positions of these series change. This particular situation is presented in Fig.1. We note that at certain  $R$  values, the states arising from two different series can overlap. Whether they strongly interfere or not depends on the strength of the coupling terms. In Fig.2, we display the resonance width as a function of internuclear distance for the lowest three resonances in the singlet  $\pi$  ungerade series(41). We note large changes at the energies at which the lowest resonance from the second series overlaps one from the first. At large values of  $R$ , all resonances below the first threshold belong to series 1. As we move the nuclei closer, the lowest resonance of series 2 drops below this threshold and begins to cross the states of the first series. At these crossing points, we have large interference effects, and the width changes dramatically. For these cases, the standard independent-resonance approximation fails. For atomic systems, the position of the series is fixed. Additional interactions such as magnetic fields must be introduced in order to vary the coupling strength. In the molecular case, we use the internuclear distance as an effective parameter to change the interaction without introducing any extra processes. We, thus, have an versatile tool to study general resonance interference effects.

Such interference effects can have profound consequences for processes like dissociative photoionization, dielectronic recombination, and dissociative recombination. In addition, Feshbach resonances can play important roles in direct molecular photoionization. In certain energy regimes, we witness pronounced changes in the asymmetry parameter,  $\beta$ , due to trapping in these compound states. While the agreement between theoretical and experimental results for the photoionization of molecular hydrogen is not extremely good, the methods(42,43) that include the resonant effects produce a general structure in the  $\beta$  parameter similar to that observed in the synchrotron data. The situation is complicated since the position and widths of the resonances depend strongly on the internuclear separation,  $R$ . Therefore, simple vibrational-averaging prescriptions may not be adequate to handle this case.

### 3.3 Allowed transitions $H_2$

The optically allowed transitions are dominated by the dipole-coupling terms of the direct interaction. These terms have long-range components that can effectively ladder-couple( $\Delta l = 1$ ) to very high partial waves. The high

partial waves are associated with large centrifugal barriers, which confine the electron to regions outside of the molecular charge cloud. Therefore, we expect that the cross sections will not be particularly sensitive to the intricacies of the short-range interactions. In Fig. 3, we present the integrated excitation cross section for the transition from the ground to first excited singlet state of molecular hydrogen:



for the Born(44), DW(13), and SV-two-state(44) cases. We note rather good agreement between the DW and SV results, confirming our original supposition that detailed treatment of the short-range interactions might not be necessary. At the higher energies, even the Born is not in great error. The comparison with experiment(45,46) might at first glance appear rather poor given the good agreement among the theoretical methods. However, the allowed transitions pose a problem in proper extrapolation of the small-angle experimental results. Since these transitions are highly influenced by the long-range, dipole coupling, they have a rapidly rising DCS at low angles. Therefore, a large contribution to the integrated cross section comes from this small-angle region. Unfortunately, this is precisely the regime in which the experimental errors are largest, thus making extrapolation a tricky affair. The same conundrum arises in the elastic scattering of electrons by strongly polar molecules(4). At angles below about ten degrees(10°) all of the theoretical methods converge to the Born result. Comparison with experiment in this span of angles would lead to an unambiguous normalization. However, by the point at which the experimental errors become small, the differences among the various theoretical calculations have become large. Thus, testing the validity of the theoretical results by using the integrated cross section can lead to incorrect conclusions. A better gauge is the DCS away from the small-angle region. In fact by comparing at angles above about thirty degrees, we find very good agreement between the SV results and the experiment even at the higher energies.

### 3.2 Forbidden Transitions $H_2$

As we mentioned above, optically forbidden transitions present a stringent test for the various scattering methods since the coupling occurs only through exchange terms and only fairly low partial waves are important. Due to the involvement of low partial waves, the electron can penetrate deeply into the molecular charge cloud and experience the full range of short-range interactions such as the strong nuclear attraction and the exchange effects. In Fig. 4, we compare RM(47), SV(37), and LA(48) methods for the transition from the ground state of molecular hydrogen to the first excited triplet state.



The LA and SV calculations were performed at the two-state CC level while the RM results included some additional correlation effects in Eq.(4a). The results are in very good agreement across a rather wide range of energies. We also display results(dot) in which the strong orthogonality constraint is imposed but no terms are introduced to relax this condition. We observe that such omissions can lead to errors on the order of a factor of two in some cases. The DW results are about thirty per cent too high and the Born-Rudge about the same amount too low. In addition, the agreement with experiment is also quite good.

### 3.4 Shape resonances

Shape resonances, which result from the trapping of an electron within a potential barrier, play important roles in elastic scattering processes. Since these resonances are generally broader than the Feshbach, they enhance the collisional cross section over a wider range of energies. How they affect the excitation process is the subject of recent calculations on oxygen and the nitrogen ion. To gain some insight into the mechanism, we imagine a two-state case. In the uncoupled representation, we assume that only the first channel has a shape resonance. As the coupling is increased, we might expect to see some notable changes in the scattering parameters for the second channel as we scan over the energy regime of the shape resonance.

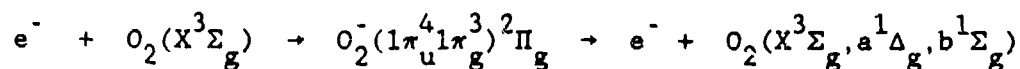
We consider electron scattering from molecular oxygen as an illustration of the effects of shape resonances on excitation processes since both close-coupling, model ERT, and experimental results are available. The ground configuration for  $O_2$ :

$$(1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 1\pi_u^4 1\pi_g^2)$$

gives rise to three electronic states:

$$X^3\Sigma_g^-, a^1\Delta_g, \text{ and } b^1\Sigma_g^+,$$

with equilibrium thresholds at 0.98 and 1.64eV respectively. An electron incident on the ground(X) state with sufficient energy can directly excite the a and b levels. However, another mechanism is also available. We have a well-known shape resonance at very low energies ( $\approx 100\text{meV}$ ) associated with attaching an electron to the open  $\pi_g$  shell. The excitation process might also go by this resonant mechanism as



Therefore, the shape resonance, which results from the addition of an electron to the ground configuration, can affect all three final channels. The situation as always is more complicated than this simple picture. For example, the resonance state can also decay by ejecting an electron from the  $\pi_u$

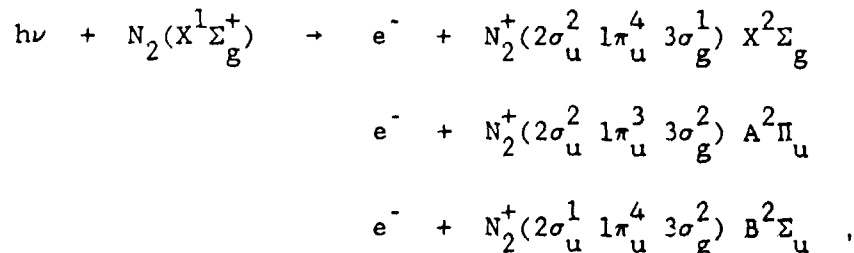
orbital. The resulting neutral configuration ( $\dots 1\pi_u^3 1\pi_g^3$ ) leads to an additional six electronic states. We thus have a rather complicated problem. In Fig. 5, we display the excitation cross sections to the a and b states as a function of electron energy. The RM(32) calculations were performed in a three-state CC format while the ERT(40) results contain the effects of the additional decay channels. We observe rather good agreement between the two theoretical calculations and in turn with experiment(50,51). That the shape resonance provides the dominant excitation mechanism is confirmed by the CC calculations whose primary contributions come from the  $^2\Pi_g$  scattering symmetry. More elaborate comparisons will have to await larger CC calculations as a function of internuclear distance. The system is a fascinating one in that a very low-lying shape resonance can influence the excitation cross section at such high energies.

A similar situation arises in the photoionization of molecular nitrogen,

which has a ground configuration of

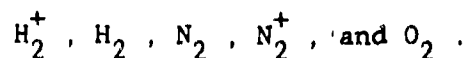
$$(1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 1\pi_u^4) X^1\Sigma_g^+.$$

If the photon has sufficient energy, three ionization channels become available:



where we have only indicated the active shells. The first channel supports a well-known  $^1\Sigma_u$  shape resonance in the range of photon energies from about 28 to 32eV. In Fig.6a, we display the eigenphase sum as a function of energy for electron scattering from the ground state(X) of the nitrogen ion in the resonance symmetry. This rise of the phase sum is a characteristic feature of a broad shape resonance. We also present in Fig.6b the photoionization cross section for leaving the ion in its ground state and note the enhancement around 35eV due to this resonance. The scattering calculation(52) was performed at the static-exchange(SE) level and therefore included no effects from the other channels. However, except in the low-energy region, where autoionization effects become important, this simple prescription reproduces the experimental cross section quite well. The situation for photoionization into the excited B state of the ion is much different. In Fig.7, we present the SE result(line) for the asymmetry parameter,  $\beta$ . We note rather large differences with the experimental results. One possible explanation centers on the shape resonance in the first channel. If the coupling between the two channels is sufficient, we might expect the resonance to influence the second process. Multiple- scattering calculations(53) gave the first indication of the validity of this conjecture. The recent two-state CC(X and B) calculations(54) of Basder and Lucchese have placed this on stronger footing as indicated by the dashed line in Fig.7. The final details must await more elaborate calculations with larger numbers of states, especially the A pi level, and with the effects of nuclear motion.

In the above examples, we have tried to illustrate the wide variety of systems and mechanisms that can now be treated with these new methods. We have tried to emphasize interesting physical processes in addition to portraying the efficacy of the approaches. To date, the "ab initio" treatments have been applied to electronic excitation of the following systems:



If we include those systems for which the electronically elastic cross sections have been calculated using closed-channels then the list grows much longer.

#### 4. CONCLUSION

In the previous section, we portrayed the power of these theoretical methods to explicate some rather complicated collisional processes. Since these *ab initio* and model techniques are in an inchoate stage, the degree of accomplishment is indeed impressive. The time is most propitious since these methods can be readily extended to larger systems and more complicated mechanisms. Pseudoresonances, which arise from the limited basis-set expansions used in all methods, still plague the excitation calculations; however, practical procedures are available to average out their effects. The extent to which the nuclear motion must be treated remains uncertain. This must await more elaborate calculations, which include nonadiabatic effects, and careful cross-comparison with experiment. Both of these cases seem tractable. Thus, we are poised at a most interesting time in the field. We might paraphrase Churchill as to our status: "this is not the end," since many mechanisms have yet to be addressed in detail; "it is not even the beginning of the end," since problems remain with existing methods and models; "but it is, perhaps, the end of the beginning," since reasonably-sized systems can be routinely treated with moderately elaborate methods.

#### ACKNOWLEDGMENTS

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# FIGURE CAPTIONS

Fig.2 Resonance widths as a function of internuclear separation,  $R$ , for  $e^- + H_2^+$  scattering in the  $^1\Pi_u$  symmetry below the first excitation threshold. Line, dash, and chain curves represent the first, second, and third lowest resonances respectively.

Fig.3 Integrated excitation cross section as a function of incident electron energy for the transition  $X^1\Sigma_g^+ \rightarrow B^1\Sigma_u^+$  in  $e^- + H_2$  scattering. Nomenclature: line - DW(13); dash - SV(44); chain - Born(44); circles - exp(46); triangles - exp.(45).

Fig.4 Impact excitation cross section as a function of electron energy for the transition  $X^1\Sigma_g^+ \rightarrow b^3\Sigma_u^+$  in  $e^- + H_2$  collisions. Nomenclature: line - LA(48); dash - RM(47); chain - SV(37); dot - LA, no relaxation; cross - exp.(54).

Fig.5 Impact excitation cross sections as a function of electron energy for  $e^- + O_2$  collisions for the transitions: a)  $X^3\Sigma_g^- \rightarrow a^1\Delta_g$  and b)  $X^3\Sigma_g^- \rightarrow b^1\Sigma_g^+$ . Nomenclature: line - RM(32); dash - ERT(40); circle - exp.(49); triangle - exp.(50).

Fig.6 a) Eigenphase sum as a function of electron energy for  $e^- + N_2^+(X^2\Sigma_g^+)$  collisions in the  $^1\Sigma_u$  resonance symmetry in the static exchange approximation. b) Photoionization cross section for  $N_2$  at the SE level leaving the ion in its ground state ( $X^2\Sigma_g^+$ ). The line represents the LA calculations(51) and the triangles, experimental results(55).

Fig.7 The asymmetry parameter,  $\beta$ , as a function of photon energy for the photoionization of  $N_2$  leaving the ion in the excited  $B^2\Sigma_u^+$  state. Nomenclature: line - one-state LA(51); dash - two-state C-functional(53); triangles - exp.(55).

# SCHEMATIC DIAGRAM OF RESONANCE POSITIONS IN $H_2$

